

# Asymmetric pulsing for reliable operation of titanium/manganite memristors

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## Abstract

We present a pulsing protocol that significantly increases the endurance of a titanium-manganite interface used as a binary memory cell. The core of this protocol is an algorithm that searches for the proper values for the set and reset pulses, canceling the drift in the resistance values. A set of experiments show the drift-free operation for more than  $10^5$  switching cycles, as well as the detrimental effect by changing the amplitude of pulses indicated by the protocol. We reproduced the results with a numerical model, which provides information on the dynamics of the oxygen vacancies during the switching cycles.

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Metal - transition metal oxide interfaces exhibiting resistive switching (RS) are prominent candidates for non volatile memory applications. Despite many appealing features like retentivity, capability of downscaling, integration in complementary metal-oxide semiconductor (CMOS) architectures and speed, one of the main drawbacks of these systems is the poor endurance.[1, 2]

It is nowadays widely accepted that the redistribution of oxygen vacancies near the metal oxide interface might determine the main features of the bipolar RS response. [1, 3–6] A recently proposed model [7], that succeeded in reproducing non trivial experimental findings [8], indicates that the migration of oxygen vacancies due to the local electric fields built up in a nanoscale vicinity of the metal oxide interface is at the origin of the most significant resistive changes. Each microscopic region of the sample has a resistivity that is a function of the local oxygen vacancy concentration. When an electrical pulse (i.e. set) is applied to the device, local electric fields proportional to the local resistivity and to the current density develop. If these fields are strong enough, the oxygen ions will move, changing the vacancies profile along the interface and hence the total resistance of the device.

After this redistribution of vacancies, a pulse with the opposite polarity (i.e reset) might not reproduce the initial profile of electric fields and then, neither the vacancies will return to the original positions, nor the device will return to the original resistance value after the completion of the pulsing cycle. The repetition of this process will produce a drift of the switching resistance levels (ON/OFF ratio) which eventually fully degrades the memory performance. The strategies reported in literature to overcome this problem are mainly based on the design of the device and the selection of materials.[1, 9–12]

In this work we present a pulsing protocol that allows to obtain more than  $10^5$  RS switching cycles in manganite-based devices, significantly improving their endurance. We compare the results with numerical simulations.

We have made RS devices of polycrystalline manganite  $\text{La}_{5/8-y}\text{Pr}_y\text{Ca}_{3/8}\text{MnO}_3$  (LPCMO) with Ti contacts[13, 14]. The devices, depicted in the inset of Fig. 1, were fabricated on a LPCMO sintered bulk 1 mm-thick with a diameter of 13 mm. The 300 nm-thick, 1.5 mm-diameter pads were sputtered through a shadow mask. The nearest distance between pads is  $\sim 2$  mm. The electrical characterization was performed with one of the Source Measurement Units (SMU) of a Keithley 2602 connected in the remote sense configuration. The SMU applies the writing (1 ms) and reading (200 ms) pulses through the A and C pads, and

measure the voltage drop between the A and B contacts. In this configuration the resistance of both A and C metal-oxide interfaces change, but only the resistance of the A interface is measured.

We define two resistance levels corresponding to two logic levels required to use the RS devices as a binary memory element, as indicated in Fig. 1. We define a high level (H) that has to be greater than  $R_{H,min}$  and a low level (L) that always has a resistance lower than  $R_{L,max} = 0.39 \cdot R_{H,min}$ . Both values are scaled depending on the device switching range. The factor 0.39 mimics the levels of the low-voltage CMOS-logic product family with translation (LCX)[15]. Defining the levels in this way introduces a gap in the resistance values. Successful RS operations are defined as those overcoming this gap.

During the experiments, the generator uses three types of current pulses: the read pulse that is used to sense the resistance of the interface, the set pulse that switches the device from the level L (low resistance) to the level H (high resistance), and the reset pulses that switches from H to L[16]. The read pulse with  $I_{RD}=50 \mu A$  is low enough to ensure that no displacement of vacancies occurs (i.e. it does not change the resistance level).

We implement an algorithm that looks for the proper values (for successful RS) for the set and reset current pulses,  $I_{SET}$  and  $I_{RST}$ , with the general criteria of keeping a low number of pulses and the lowest possible amplitude. The algorithm, tries to set the logic state by applying a single current pulse  $I'_{SET}$ . If it fails (i.e. it does not overcome the resistance gap), a second identical pulse is applied in order to set the state. If this second attempt fails, the value of  $I'_{SET}$  is increased and the algorithm continues applying pulses with increasing value until it eventually succeeds. The current is increased in steps. The values of these steps is fixed through all the experiment and is set in a few percent of the expected switching current, typically 5-10%. The device is considered defective if after increasing the current value 50 times, the resistance level does not change. If five consecutive set procedures require these second chances then  $I'_{SET}$  will be increased anyway. An analogous criteria is applied for the reset procedure. Eventually the algorithm finds two independent values for  $I_{SET}$  and  $I_{RST}$  required for stable operation. [17]

Fig. 2 shows the initial stage of a typical experiment. Statistically, the correction to the amplitude of the pulses ceases within the first 3000 cycles, reaching a ratio  $|I_{SET}/I_{RST}| = 2.6 \pm 1.2$ . Even if after these first corrections the amplitude of the pulses require no further corrections, once every  $5400 \pm 300$  switching attempts it is necessary to apply a second pulse

in order to properly switch the device. The histogram presented in Fig. 1 depicts the typical distribution of the resistance values when switching the device with the proposed protocol during 120000 cycles. Notice that the present protocol produces no events in the gap.

With the aim of experimentally testing the robustness of the above described asymmetric pulsing protocol we performed a series of experiments to show the effect of deliberately changing the ratio  $I_{\text{SET}}/I_{\text{RST}}$  attained by the protocol (Fig. 3). The devices in these experiments correspond to different location of the contacts on the same sample of LPCMO. At the beginning of this set of tests, they were switched a minimum of 3000 cycles (only the last 300 are shown) in order to achieve the proper  $I_{\text{SET}}/I_{\text{RST}}$ , depending on the selected contacts. As a reference, Fig. 3a shows a device that has remained in operation under the same conditions 700 cycles more. In the device of Fig. 3b, we stopped the operation of the algorithm and increased the amplitude of  $I_{\text{RST}}$  at the cycle indicated with the number 0. This reduction of the  $I_{\text{SET}}/I_{\text{RST}}$  ratio, results in an evident drift of the resistance values and the H resistance value level eventually falls inside the gap, i.e. the device no longer switches between the pre-defined levels. For Fig. 3c the  $|I_{\text{SET}}/I_{\text{RST}}|$  ratio was increased by a factor 1.5, producing the complementary drift effect.

We successfully reproduced the experimental results employing the model introduced in Ref. [7], which is based on the electric field enhanced oxygen vacancy diffusion dynamics.[18] In this model the active region for conduction is a one dimensional resistive network, in which each site corresponds to a (nanoscale) domain, having a local resistivity proportional to the local density of oxygen vacancies,  $\delta_i$ . The dynamic for the vacancies is governed by the equation:

$$p_{i,i+1} = \delta_i (1 - \delta_{i+1}) \exp(-V_o + \Delta V_i) ,$$

that specifies the probability for transfer of vacancies between two neighboring sites.  $V_o$  is a dimensionless constant related to the activation energy for vacancies diffusion and  $\Delta V_i$  is the local potential drop  $\Delta V_i(t) = V_{i+1}(t) - V_i(t)$  due to the applied electric pulse. For the present analysis we consider one interface (I) in contact with the bulk (B) of the sample. The local resistivity at site  $i$  is given by

$$\rho_i = \delta_i \cdot \left( A_B + \frac{A_I - A_B}{1 + \exp\left(\frac{i - N_I}{w}\right)} \right) ,$$

where  $A_B$  and  $A_I$  relate vacancy concentration and resistivity in the bulk and in the interface region respectively ( $A_B \ll A_I$ ), and  $N_I$  and  $w$  define the length and the width of the interface. First, we simulated the application of triangular sweeps to a flat distribution of vacancies, obtaining hysteresis switching loops similar to those presented in Ref [8]. This step emulated the forming process and provided information on the resistance switching range of the simulated sample. Then, we simulated the proposed pulsing protocol. We successfully reproduced the continuous cycling between the L and H states without drift.

The simulation eventually arrived to a stable operation, applying asymmetrical pulses as in the experiments. For the actual parameters of the simulation we obtained a ratio  $|I_{SET}/I_{RST}| = 2.9$  that smoothly depends on  $w$ , but a systematic study of this phenomena is out of the scope of this work. In stable operation both L and H states correspond to two well defined profiles of vacancies,  $\bar{\delta}_H$  and  $\bar{\delta}_L$ . The electrical pulses produce a redistribution of vacancies  $\bar{\delta}_{H(L)} \xrightarrow{I_{pulse}} \bar{\delta}'_{H(L)}(I_{pulse})$ , and a subsequent change in the total resistance of the device  $R_{H(L)}(\bar{\delta}_{H(L)}) \xrightarrow{I_{pulse}} R'_{H(L)}(I_{pulse}, \bar{\delta}'_{H(L)})$ . Fig. 4 presents the calculated  $R'_{H(L)}(I_{pulse}, \bar{\delta}'_{H(L)})$ , which was obtained by simulating the application of pulses of different intensity to  $\bar{\delta}_H$  and  $\bar{\delta}_L$ . The stable operation is the convergence of  $I_{SET}$  and  $I_{RST}$  to values where  $\bar{\delta}'_L = \bar{\delta}_H$  and  $\bar{\delta}'_H = \bar{\delta}_L$ . This condition is presented in Fig. 4:  $R'_H$  equals  $R_L$  when the amplitude of the pulses is  $I_{RST}$  and  $R'_L = R_H$  for pulses of amplitude  $I_{SET} = -2.9 \cdot I_{RST}$ . The lack of symmetry explains the need of non-symmetric pulses to obtain a stable operation. The drift of the resistance upon symmetric pulsing is due to the gradual injection of vacancies deeply into the bulk where they get stuck never returning to the interface region. The local electric field,  $\Delta V_i \propto I_{SET(RST)}$ , is much lower in the bulk region than in the interface. As a consequence, the amount of vacancies in the interface gradually decreases with the repetitive cycles, with the concomitant reduction of the interface resistance. In order that all the vacancies that were injected into the bulk region during the former set pulse return to the interface during a subsequent reset pulse, it is necessary to apply a higher current pulse. If this second current pulse is stronger than required for a drift-free operation, then the amount of vacancies in the interface will be slowly increased in each cycle, with the subsequent increment of the interface resistance.

In conclusion we have proposed an experimental current protocol based on asymmetric pulsing, that succeeds in finding a stable and repetitive switching between H and L resistance states up to  $10^5$  cycles, improving the endurance of the system by means of virtually canceling

the drift in the resistance values. The theoretical model provides a physical explanation of the interface resistance degradation in terms of the injection of vacancies in the bulk region. The proposed current protocol applied to the model simulations successfully reproduces the experimental findings, validating the model hypothesis and its usefulness as a valuable aid in the analysis of the experimental results.

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- [16] Notice this is not the standard definition of low and high levels in RS.
- [17] See supplemental material at [URL will be inserted by AIP] for details about the algorithm.
- [18] See supplemental material at [URL will be inserted by AIP] for details on the model simulations.

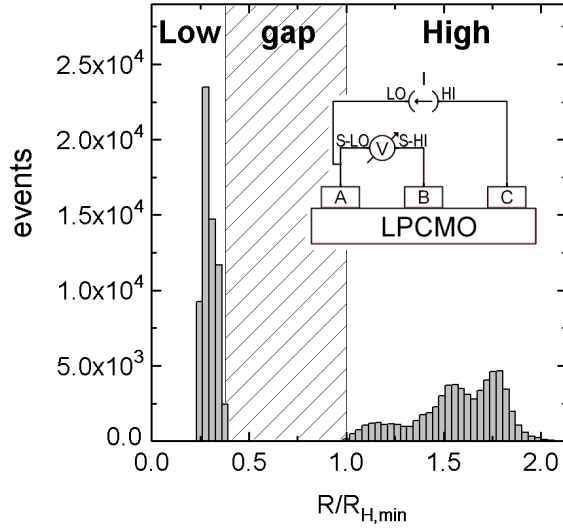


Figure .1: Histogram of the resistance values in a typical experiment with the definition the H and L levels. The inset shows the experimental setup.

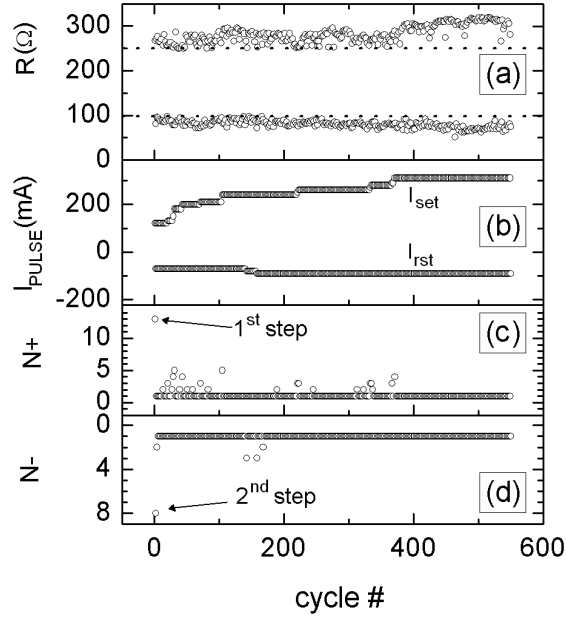


Figure .2: Initial stage of a typical experiment. The threshold levels were set to  $R_{H,min} = 254\Omega$  and  $R_{L,max} = R_{H,min}/0.39 = 100\Omega$ , values compatible with the resistance switching capabilities of the device (a). The switching protocol starts with the sample in low resistance level. In the first step, it looks for proper pulse amplitude to set the device, requiring in this case  $N_{+} = 14$  positive pulses of increasing amplitude to overcome the  $R_{H,min}$  level (c). The amplitude of the 14<sup>th</sup> pulse was  $+110mA$  (b). In the second step,  $N_{-} = 8$  negative pulses of increasing amplitude have been needed to reset the device (d), and so on. After  $\sim 400$  cycles the correction to the pulsing amplitudes ceases, reaching a ratio  $I_{SET}/I_{RST} = 310mA / -90mA$ .



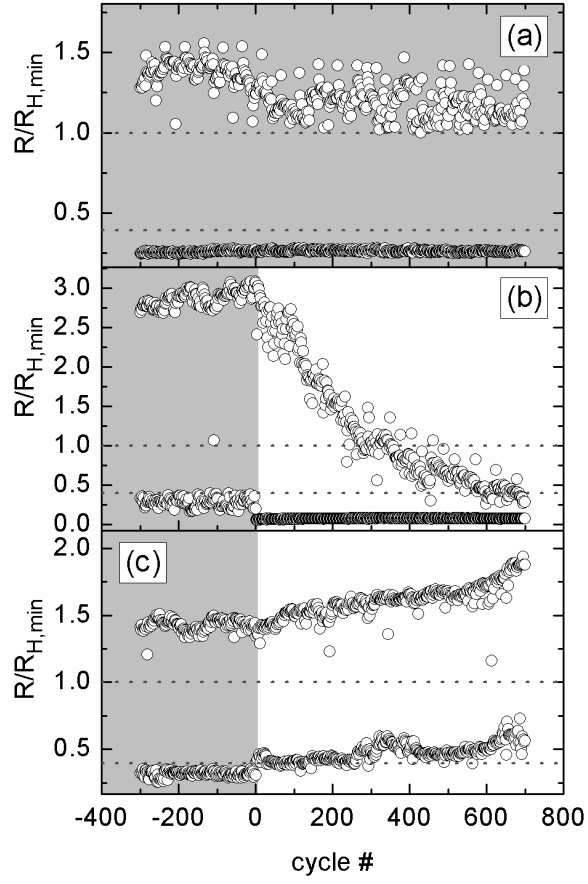


Figure .3: Effect of changing the  $I_{\text{SET}}/I_{\text{RST}}$  ratio when the device is in stable operation. Shaded in gray, the region were program operates. The horizontal dotted lines indicate  $R_{L,max}$  and  $R_{H,min}$  values. a) figure for reference, no change in the  $I_{\text{SET}}/I_{\text{RST}}$  ratio. b) the initial  $I_{\text{SET}}/I_{\text{RST}} = 110/-20$  changed to  $110/-90$  at cycle #0. c)  $I_{\text{SET}}/I_{\text{RST}}$  changed from  $310/-90$  to  $310/-60$ .

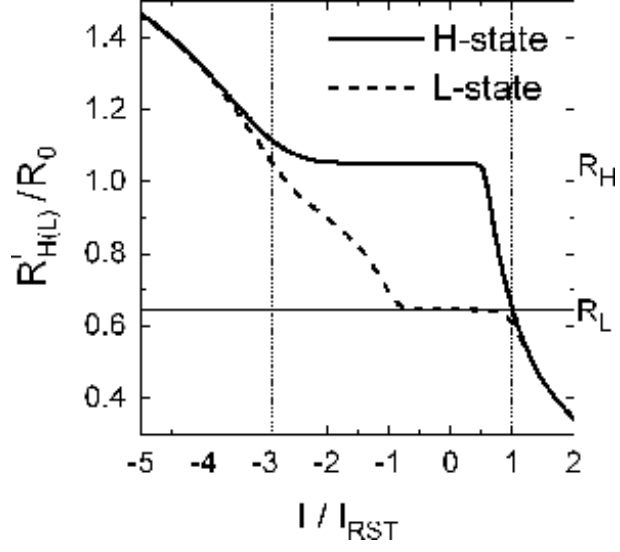


Figure 4: Model simulation of the achieved resistance for stable operation. The pulse amplitude required to change the vacancy distribution of the L state to the vacancy distribution of the H state is  $I_{SET} = -2.9 \cdot I_{RST}$ . The resistance values are normalized to the resistance of a sample with the same number of vacancies uniformly distributed,  $R_0$ .